pendence of the rate of reaction and the explosion limit on size of vessel, activity of the wall, inert gases and temperature, have been investigated. The reaction affords another example in which *chains are initiated at the wall and are propagated thence into the gas phase.* In the proposed mechanism the OH radical is believed to be the carrier in these reaction chains.

The effect of hydrogen chloride on the bromine sensitized ozone decomposition and its reaction with ozone have been studied. Very small amounts of hydrogen chloride prevent explosions in the former, while its reaction with ozone seems to be confined to a wall reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY THE IODINE–IODIDE COUPLE AT 25°

BY HERMAN A. LIEBHAFSKY

RECEIVED DECEMBER 7, 1931 PUBLISHED MAY 7, 1932

Introduction

The reaction system comprising hydrogen peroxide, iodine and iodide ion in neutral and dilute acid solutions has provided the material for a series of investigations extending over some three-fourths of a century, and culminating in the intensive work of Abel.[1] With the last of his papers on the subject, it seemed that these investigations could be regarded as complete, and that this reaction system, while apparently similar to the bromine–bromide system investigated by Bray and Livingston,[2] was in reality much more complex. In establishing a mechanism for this complex system, Abel deduced for the specific rate of the hydrolysis of iodine (into hypoiodous and hydriodic acids) a value which has proved irreconcilable with related experimental results.[3] The iodine–iodide reaction system is therefore being re-investigated over a wide range of experimental conditions: that part of the investigation dealing with the pure catalytic decomposition of hydrogen peroxide by the iodine–iodide couple is presented here.

Rate Measurements at the Steady State.—Within a short time after hydrogen peroxide is added to a netural solution of iodide ion, a *steady state* is reached, in which the main reaction is the catalytic decomposition of hydrogen peroxide

$$H_2O_2 = H_2O + {}^1/_2O_2 \qquad (1)$$

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[1] (a) Abel, *Z. physik. Chem.*, **136**, 16 (1928); (b) *ibid.*, **96**, 1 (1920). For a comprehensive historical summary of earlier work by Abel and others, the reader is referred to Ref. 1b.

[2] Bray and Livingston, THIS JOURNAL, **45**, 1251 (1923).

[3] (a) Liebhafsky, *Z. physik. Chem.*, **155**, 289 (1931); (b) THIS JOURNAL, **53**, 2074 (1931).

The establishing of this steady state is accompanied by an increase in the rate of oxygen evolution, which is initially zero, to the value determined at any temperature by the concentrations of the substances reacting at the steady state. After this rapid initial increase, the rate of oxygen evolution furnishes a convenient measure of the rate at which the catalysis, Reaction 1, proceeds. The results of a series of measurements show that the rate law for this evolution of oxygen[4] is

$$+\frac{dO_2}{dt} = kH_2O_2 \text{ or } -\frac{d(H_2O_2)}{dt} = k(H_2O_2) \qquad (2)$$

that is, the catalytic decomposition of hydrogen peroxide by the iodine–iodide couple is always first order with respect to hydrogen peroxide.

The apparatus in Fig. 1 was patterned after that of Abel.[1b] The reaction mixture was stirred in a one-liter flask, indentations in which served as baffles. The evolved oxygen was measured in a gas buret attached to B; initial time was taken when the peroxide, added by inverting the cup A, hit the solution.

With a 400-cc. reaction mixture and moderate rates of oxygen evolution, the results depended on the rate of stirring only when this was below 900 r. p. m. When oxygen was evolved faster than 50 cc. per minute, as in experiments at high concentrations of iodide ion, where approximately half the peroxide decomposed in the first minute, accurate results were not obtained even with stirring above 1500 r. p. m.; irregularities in such results (*cf.* the right-hand side of Fig. 3) were attributed to supersaturation. For experiments at low (I^-), the addition of sand effectively prevented supersaturation.

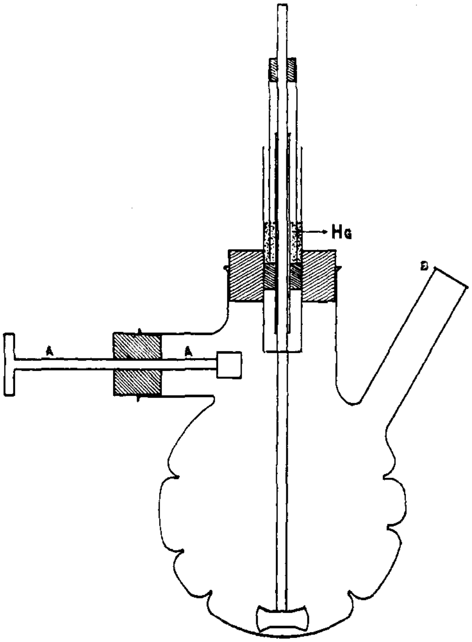

Fig. 1.—Gas evolution apparatus.

For measurements at (I^-) below 10^{-2} *M* (*cf.* the left-hand side of Fig. 3) an accurate value for the rate of oxygen evolution was obtained before

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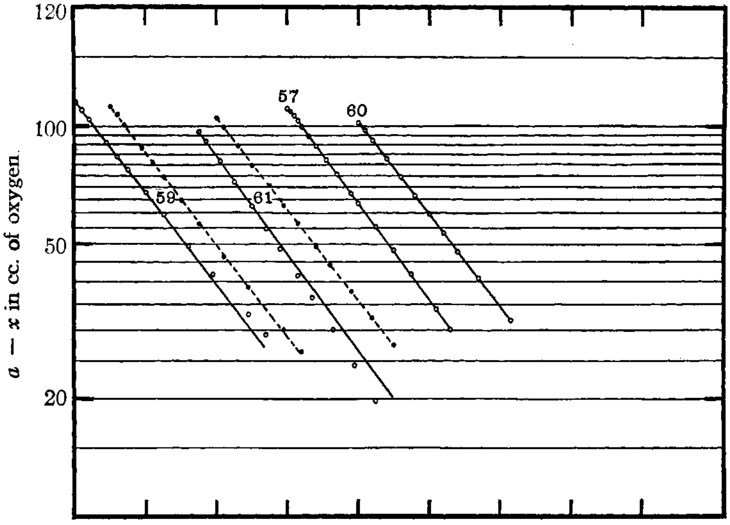
[4] Since Equation 2 expresses the rate law for a first-order reaction, the value of k is independent of mass units, provided the same unit is employed throughout. k has therefore the same value in both the formulations given above. ( ) denotes "concentration of" in moles/liter; formulas alone denote quantities.

(H_2O_2) had sensibly changed, and k was taken as the quotient of this rate by the concentration of hydrogen peroxide. For experiments at higher (I^-) the following integral method was used in evaluating k. If x represents the cc. of oxygen evolved in such an experiment at an arbitrary time, t, and a represents the value of x when the reaction has gone to completion, then $k/2.30$ is the slope of the line obtained by plotting $a - x$ as ordinate on *semi-logarithmic* paper against t as abscissa. To illustrate this method of plotting and to demonstrate that Reaction 1 is first order with respect to hydrogen peroxide, the results of several experiments are given in Fig. 2.[5] Initial time is placed farther to the right for each experiment in order to prevent crowding.



Time scale: 1 division = 20 minutes.

Fig. 2.—Typical rate experiments. (The plot is on semi-logarithmic paper. k values from these experiments are plotted on Curve II, Fig. 4.)

In Fig. 2, two experiments (Nos. 57 and 60) obey perfectly the first order rate law (Equation 2); the points of No. 61 show a downward, and those of No. 59 an upward, trend as the reaction nears completion. When the a values for these two experiments are properly corrected by the number of cc. of oxygen corresponding to the distance of the last point from the solid line, (for No. 61 a is increased by 8 cc., while for No. 59 a is decreased by 3 cc.) these trends disappear entirely as the broken lines,

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[5] It may be pointed out here that the validity of Equation 2 is a sufficient proof that Reaction 1 is the main reaction taking place in the system, for Equation 2 shows that no substance in the system except hydrogen peroxide undergoes a concentration change in the course of the reaction, and it is stoichiometrically impossible to have this condition fulfilled and produce oxygen from hydrogen peroxide except by Reaction 1.

which have been plotted using the corrected a values, show. Such corrections eliminated both positive and negative trends, and, in general, left the value of k practically unaltered. Deviations from Equation 2 were therefore regarded as due only to errors in the experimentally measured value of a caused, for example, by a change in room temperature during the course of an experiment. Measurements were suspended in the slower experiments when these were approximately three-fourths complete, but more rapid experiments often showed Equation 2 to be obeyed within several per cent. of completion.

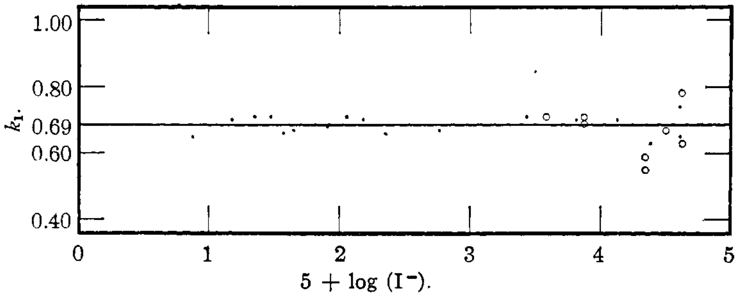

Fig. 3.—Summary of rate measurements in initially neutral iodide solutions: •, KI solutions; ⊙, NaI solutions.

From the results of previous investigations[1b,6] it was expected that in (nearly) neutral solution the complete differential equation for the rate at which hydrogen peroxide is catalytically decomposed would be

$$-\frac{d(H_2O_2)}{dt} = k'(H_2O_2)(I^-) \tag{3}$$

corresponding to the reaction

$$H_2O_2 + I^- \xrightarrow{k_1} IO^- + H_2O \tag{4}$$

by which hydrogen peroxide is reduced at the steady state. Since one mole of hydrogen peroxide is oxidized for every mole thus reduced, then, for the same concentrations of peroxide and iodide ion, $-(d(H_2O_2)/dt)$ in Equation 3 will be twice as great as $-(d(H_2O_2)/dt)$ for Reaction 4 at a distance from the steady state. It follows, therefore, that k' will be twice k_1, the specific rate constant for Reaction 4; or

$$k_1 = \frac{k'}{2} = \frac{k}{2(I^-)} \tag{5}$$

The rate at which hydrogen peroxide is reduced at the steady state by iodide ion may now be written as

$$-\frac{d(H_2O_2)}{dt} = k_1(H_2O_2)(I^-) \tag{6}$$

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[6] (a) Among others, Walton, *Z. physik. Chem.*, **47**, 185 (1904); (b) Noyes, *ibid.*, **18**, 118 (1895).

The k_1 values plotted in Fig. 3 against log $(I^-) + 5$ as abscissa were obtained at 25° from measurements on a series of initially neutral reaction mixtures; the constancy of k_1 means that Reaction 4 is subject to practically zero salt effect when (I^-) is below 0.1 *M* and the ionic strength of the reaction system is at a minimum. That this is no longer true when foreign salts are present will be apparent from the k_1 values given in a later section (*cf.* Fig. 4). The value $k_1 = 0.69$ is in almost perfect agreement with the value $1.34/2 = 0.67$, which was obtained by Walton (Ref. 6a, Table 6) from similar experiments over a much smaller concentration range. The value given by Abel for a reaction system containing acetate ion is somewhat higher (Ref. 1b, page 26, has $k_1 = 1.57/2 = 0.78$), probably mainly because the degree of dissociation of potassium iodide as obtained from conductivity measurements was used in its evaluation. Noyes[6b] finds, by following the rate of iodine formation in solutions of varying acid concentration, that $k_1 = 0.68$ to 0.82. Since this variation of k_1 is in the form of a trend with (H^+) which may be attributed (as Bray, *Z. physik. Chem.*, **54**, 463 (1906) has shown) to a third-order reaction

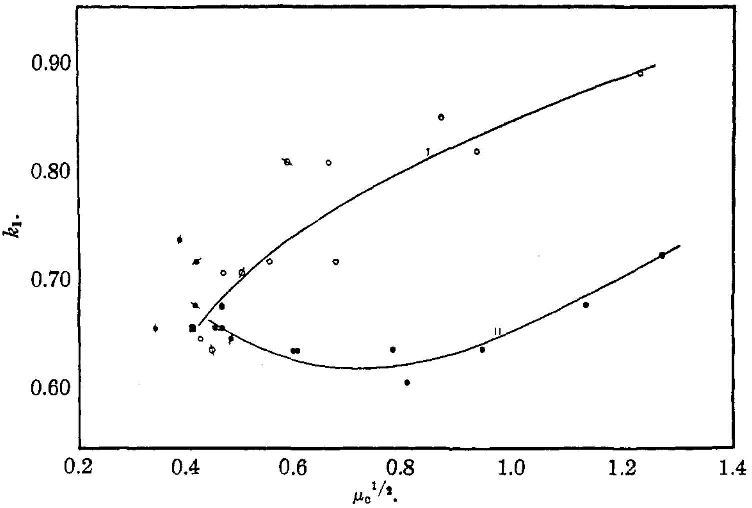

Fig. 4.—Variation of k_1 with ionic strength in the presence of Sörensen phosphate buffer. (Added salt: ○, $NaClO_4$ (Curve I); ●, Na_2SO_4 (Curve II); ϕ, KI, and ♦, phosphate buffer only. ■ is the initial point for Curves I and II, and corresponds to a reaction mixture in which $a_{H^+} = 1.01(10^{-7})$ and $(I^-) = 0.0215$).

$$H_2O_2 + H^+ + I^- = HIO + H_2O$$

negligible in our reaction system, Noyes' value also is in good agreement with the result of the present investigation.

The theory of the hydrogen peroxide catalysis[1a,2] requires that there be, in addition to Reaction 4, a compensating reaction in which hydrogen peroxide is oxidized. The simplest one that has been suggested is the oxidation of H_2O_2 by IO^-, a product in Reaction 4

$$IO^- + H_2O_2 \longrightarrow I^- + H_2O_2 + O_2 \qquad (7)$$

Hypoiodite ion will exist in the reaction system at an extremely low concentration, always governed at the steady state by the equilibrium

$$I_2 + H_2O \rightleftharpoons IO^- + I^- + 2H^+ \qquad (8)$$

From Equations 7 and 8 it is apparent, therefore, that the absolute rate at which hydrogen peroxide is oxidized at the steady state may be written

$$-\frac{d(H_2O_2)}{dt} = k_2(IO^-)(H_2O_2) = k_2' \frac{(I_2)}{(I^-)(a_{H^+})^2\gamma_{I^-}\gamma_{IO^-}}(H_2O_2) \qquad (9)$$

In this expression k_2' is the product of k_2, the specific rate constant for Reaction 7, by K', the equilibrium constant for Reaction 8. Since no suitable values for the activity coefficients γ_{I^-} and γ_{IO^-} are available, Equation 9 will be written in the convenient form

$$-\frac{d(H_2O_2)}{dt} = k_2' \frac{(I_2)}{(I^-)(a_{H^+})^2}(H_2O_2) \qquad (9a)$$

We shall see later that the kinetic interpretation of our results does not depend upon this approximate formulation of Equation 9.

When the steady state has been reached, the rate at which hydrogen peroxide is reduced (Equation 3) is equal to the rate at which it is oxidized according to Equation 9a if *hypoiodite ion alone* oxidizes the peroxide. Subject to this condition, we may write

$$k_1(H_2O_2)(I^-) = k_2' \frac{(I_2)}{(I^-)(a_{H^+})^2}(H_2O_2) \qquad (10)$$

and

$$\frac{k_2'}{k_1} = \frac{(I^-)^2(a_{H^+})^2}{(I_2)} = F \qquad (11)$$

A sufficient constancy of F over a wide range of experimental conditions may thus serve as a test for the assumption that hydrogen peroxide is oxidized by hypoiodite ion alone. It may be pointed out here that F has the form of the steady state function found by Bray and Livingston for the bromine–bromide catalysis[7] where the hypohalous acid, and not the corresponding ion, was involved in both compensating reactions.

Concentration Measurements at the Steady State.—When hydrogen peroxide is added to an initially neutral solution of iodide ion, the approach to the steady state is characterized by the oxidation of a small amount of iodide according to the stoichiometric equation

$$3I^- + H_2O_2 = I_3^- + 2OH^- \qquad (12)$$

consequently, the solution becomes slightly alkaline. The accurate determination of F is most conveniently accomplished with the use of buffer

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[7] *Cf.* Ref 2, p. 1262.

solutions, for then the activity of hydrogen ion at the steady state can be calculated with some degree of accuracy. When the initial concentration, $(I^-)_i$, of iodide ion in a reaction mixture at the steady state is known, and the total amount of oxidized iodide, $\Sigma(I_2)$, $\Sigma(I_2) = (I_2) + (I_3^-)$ has been determined by titration, the value of F may be calculated. In making this calculation, the equilibrium

$$I^- + I_2 \rightleftharpoons I_3^- \quad (13)$$

must be considered; $(I_2)(I^-)/(I_3^-) = 0.00140$ at 25°[8] was employed throughout in calculating (I_2) and (I^-). Any change of buffer in the approach to the steady state is, of course, governed by stoichiometric relations similar to those in Equation 12; the hydrogen ion activity used in the calculation of F was always that corresponding to the buffer solution actually present at the steady state.

For most experiments $\Sigma(I_2)$ was determined by titration with thiosulfate after all of the peroxide had been decomposed. For experiments in which this decomposition was very slow, however, it was often necessary to titrate while peroxide was still present: this could be accomplished satisfactorily when both (H_2O_2) and (I^-) were so low that no appreciable oxidation of iodide ion took place during titration. Such oxidation could always be detected by an "afterbluing" of the solution when the starch end-point had once been reached. At these low concentrations of hydrogen peroxide, blank experiments showed no evidence of reaction between the peroxide and thiosulfate. In general, sufficient (two or more) determinations to ensure a reliable value of $\Sigma(I_2)$ were made for each steady state mixture.

The results of three series of such experiments are listed in Table I in which all data except the initial concentrations of iodide ion, $(I^-)_i$, are for the steady state. The values of a_{H^+} for Table Ia were obtained from the expression

$$P_H = -\log a_{H^+} = 4.73 + \log \frac{\text{acetate ion}}{\text{acetic acid}} + \log \gamma \quad (14)$$

given by Cohn, Heyroth and Menkin;[9] the γ values given by the authors for buffer solutions M in total acetate and containing no other salt were employed in the calculation. In Table Ib,[10] values of a_{H^+} were calculated

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[8] Jones and Kaplan, This Journal, **50**, 1485 (1928).

[9] Cohn, Heyroth and Menkin, (a) *ibid.*, **50**, 696 (1928); (b) *ibid.*, **49**, 173 (1927).

[10] The experiments in Table Ib were carried out after a similar series, which is not published, to conserve space, employing Sörensen's phosphate solutions (see Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1928, p. 210) had been completed; values of F calculated from the latter varied from 0.8 (10^{-12}) to 1.8 (10^{-12}), and showed a positive trend with increasing (I^-). These variations were probably due in part to uncertainties in the calculated values of a_{H^+}, for with the Sörensen buffer (in which total phosphate is only 1/15 M) large changes in a_{H^+} often took place in the approach to the steady state.

from the apparent dissociation constants given by Cohn (Ref. 9b, Table VI); the effect of added salt on the buffer was again neglected. For experiments with a_{H^+} below 10^{-4} *M*, the values of *F* in Table I show no systematic variation with the concentration of any substance; indeed, all these values (except the first two in Table Ib, which are inaccurate)

TABLE I

CONCENTRATION MEASUREMENTS AT THE STEADY STATE[a]

(a) Measurements in Acetic Acid–Acetate Ion Buffer Solution (Total Acetate is 1 *M*)

Expt.	$a_{H^+}(10^5)$	$(I^-)_i(10^2)$	$(I_2)(10^3)$	$(I^-)(10^2)$	$(I_2)(10^4)$	$F = \frac{(a_{H^+})^2(I^-)^2}{(I_2)}(10^{12})$	μ_c
88	0.200	3.12	5.65	1.47	4.91	1.8	0.93
92	.234	0.780	0.576	0.622	1.01	2.1	.91
93	.39	.780	.835	.546	1.71	2.7	.86
89	.57	.780	1.060	.486	2.37	3.2	.81
90	1.01	.780	1.495	.372	4.08	3.5	.71
91	1.62	.234	0.352	.145	1.73	3.2	.60
87	2.50	.0780	.084	.059	0.59	[3.7]	.50
95	3.80	.390	1.092	.121	5.85	3.6	.40
96	6.00	.390	1.275	.087	7.87	3.5	.30
97	10.3	.390	1.438	.0590	10.1	3.6	.20
110	10.3	.388	1.442	.0580	10.2	3.5	.20
123	10.3	.388	1.424	.0600	9.95	3.8	.20
111	14.4	.388	1.504	.0480	11.25	4.3	.15
124	14.4	.388	1.509	.0475	11.25	4.2	.15
112, 125	22.6	.388	1.603	.0350	12.85	4.9	.10

[a] Inaccurate values are enclosed in brackets. All measurements were carried out at 25°. KI and KI_3 were considered as completely ionized.

(b) Measurements in Potassium Phosphate Buffer Solutions (Total Phosphate is 0.2 *M*)

Expt.	$a_{H^+}(10^7)$	$(I^-)_i(10^2)$	$\Sigma(I_2)(10^3)$	$(I^-)(10^2)$	$(I_2)(10^4)$	$F = \frac{(a_{H^+})^2(I^-)^2}{(I_2)}(10^{12})$
152	19.0	0.187	0.0052	0.186	0.022	[6]
153	19.0	.124	.0018	.123	.0096	[6]
155	16.3	1.56	1.36	1.29	1.33	3.3
150	2.06	1.56	0.050	1.55	0.041	2.5
159	2.05	3.12	.36	3.11	.155	2.6
149	1.98	4.68	1.02	4.39	.314	2.4
148	1.82	7.80	3.20	6.85	.64	2.4
145	1.71	12.58	9.69	10.66	1.26	2.6
146	1.42	23.40	33.4	18.25	2.54	2.6
151	1.37	15.4	10.0	12.4	1.11	2.6
147	0.694	Iodine added initially	144.2	49.0	4.11	2.8
158	.218	15.4	0.40	15.3	0.036	3.1
157	.171	31.2	2.17	31.1	.097	2.9
160	.114	Iodine added initially	13.89	78.2	.248	3.2
156	.078	78.0	6.26	76.1	.115	3.1

remain within a two-fold range while the product $(a_{H^+})^2$ $(I^-)^2$ varies 10^{12}-fold: under these experimental conditions, therefore, the assumption that *hypoiodite ion alone* oxidizes hydrogen peroxide appears justified.

In interpreting the experiments for which a_{H^+} is greater than 10^{-4}, we must remember that from No. 89 to No. 123, Table Ia,[11] the value $F = 3.5\ (10^{-12})$ has been fairly well maintained despite a variation in the ionic strength, μ_c, from 0.81 to 0.20. That the increase in the values of F for the last four experiments might be due to a change in the ionic strength thus seems extremely improbable; consequently this variation will be treated as possessing a kinetic significance. The experimental data in Table Ia may, for the purpose of deducing a mechanism, be represented by the equation

$$F = 3.5(10^{-12}) + 1(10^{-8})(a_{H^+}) \qquad (15)$$

which will give the value of F in acetate buffer solution when the concentration of acetate ion is not above 0.8 M and no other electrolyte is present at high concentration. The first term is probably accurate to ±5%, but the second must be regarded as an approximate upper limit only. Equation 15 is to be compared with the equation

$$F = 1.4(10^{-12}) + 1.3(10^{-7})(H^+) \text{ at } \mu_c = 0.4 \qquad (16)$$

which Abel obtained from similar experimental results in the region of hydrogen-ion concentrations $2(10^{-5})$–$2(10^{-7})$ M. The first six experiments of Table Ia lie in this region of acid concentrations; the F_A values calculated for these experiments by the substitution of their a_{H^+} values for (H^+) in Equation 16 are in substantial agreement with the F values of Table Ia. For the remaining experiments in the table, however, F_A thus calculated becomes increasingly larger than F as a_{H^+} increases, until for Experiments 112 and 125 F_A is over *six* times as large as the value $F = 4.8(10^{-12})$ experimentally obtained.[12]

[11] Certain of the experiments at the three highest values of a_{H^+} in Table I showed a pronounced decrease in $\Sigma(I_2)$ several hours after the steady state had been reached; to determine whether this decrease might be justifiably interpreted as an *increase* in F with increasing a_{H^+}, several reaction mixtures were prepared by adding hydrogen peroxide to the acetate buffer solution in equilibrium with finely divided iodine. For these reaction mixtures $(I_2) = 0.00132\ M$, and $(I^-) = (0.00140/0.00132)[\Sigma(I_2) - 0.00132]$. A decrease in $\Sigma(I_2)$ therefore means a decrease in (I^-); and, since a_{H^+} and (I_2) are constant, a decrease in F as well. Since such decreases were observed, this disappearance of iodine must be due to a factor not properly a part of the iodine–iodide system. Subsequent analyses proved the iodine to have been oxidized; it would seem, therefore, that the oxidation of iodine to iodate ion by hydrogen peroxide proceeds at lower values of (H^+) and with shorter induction periods when acetic, instead of perchloric (*cf.* Ref. 3b, Table V; these perchloric acid solutions were not buffered) acid is used. It may be worth pointing out, finally, that the occurrence of this oxidation was quite erratic, and that Table I contains for every value of a_{H^+} at least one experiment in which no such oxidation took place.

[12] See Ref. 1a. Abel calculated (H^+) from the dissociation constant for acetic acid; the concentration of acetate ion in his system was for most experiments 0.4 M.

To show, as Abel[1a] has already done, that the second term of Equation 15 may be attributed to the oxidation of hydrogen peroxide by hypoiodous acid, we need only to trace backward the reasoning by which Equation 11 was obtained. The steady state function corresponding to this term may obviously be written

$$F' = \frac{(a_{\mathrm{H}^+})(\mathrm{I}^-)^2}{(\mathrm{I}_2)} = \frac{\kappa_2}{k_1} = 1(10^{-8}) \qquad (17)$$

The concentration of hypoiodous acid at the steady state is governed by the equilibrium

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^- \qquad (18)$$

and hence the rate law for the reaction

$$HIO + H_2O_2 \longrightarrow H^+ + I^- + H_2O + O_2 \qquad (19)$$

may be given the form (*cf.* Equations 9 and 9a)

$$-\frac{d(H_2O_2)}{dt} = \kappa_2(HIO)(H_2O_2) = \kappa_2' \frac{(I_2)}{(a_{\mathrm{H}^+})(I^-)}(H_2O_2) \qquad (20)$$

κ_2', thus defined is the product of κ_2, the specific rate constant for Reaction 19 by K, the equilibrium constant for Reaction 18.

The values $K = 3(10^{-13})$,[13] $K' = 6(10^{-24})$[14] and $k_1 = 0.69$ will now be used to calculate k_2, the specific rate of Reaction 7, and the order of magnitude of κ_2. For 25° we obtain

$$k_2 = \frac{Fk_1}{K'} = 4(10^{11})$$

and

$$\kappa_2 = \frac{F'k_1}{K} < 2(10^4)$$

These values of k_2 and κ_2, deduced from Equation 15, naturally differ from those ((10^{11}) and $3.3(10^5)$, respectively) similarly deduced by Abel from Equation 16.[1a] Measurements of Reactions 7 and 19 at a distance from the steady state have been undertaken in this Laboratory in the hope that these may confirm the value of k_2, and establish more accurately the value of κ_2.

Effect on the Reaction System of Changing the Ionic Strength.—In Fig. 4 data are given to show the effect on k_1 of changing μ_c, the ionic strength expressed in moles/liter, by adding various salts. Curve I ($NaClO_4$) and Curve II (Na_2SO_4) both embody the results of two independent series of experiments on reaction mixtures of the composition given below Fig. 4, and to which known amounts of the proper salt were suc-

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[13] Bray and Connolly, THIS JOURNAL, **33**, 1485 (1911).

[14] K' is obviously the product of K by the dissociation constant of HIO. The value

$$\frac{(H^+)(IO^-)}{(HIO)} = 2(10^{-11}) - 3(10^{-11})$$

is given by Fürth, *Z. Elektrochem.*, **28**, 57 (1922). We shall take $K' = 3(10^{-13}) \times 2(10^{-11}) = 6(10^{-24})$.

cessively added. Of the potassium iodide points, only those corresponding to the lower iodide concentrations are thoroughly reliable because of inaccuracies previously mentioned (*cf.* Fig. 3). The points in which only the phosphate buffer was changed (total phosphate is always 1/15 M) show a marked salt effect for a relatively small change in μ_c; in interpreting these data, it is important to remember that the most basic buffer mixture, which is almost pure Na_2HPO_4 solution, has a value of μ_c not very much greater than the most acid mixture, which is almost pure KH_2PO_4 solution. The phosphate points therefore represent the superposition of two salt effects, one for each type of phosphate. All the results of Fig. 4 may be summarized in the statement that the separate addition of various salts to the reaction mixture produces on k_1 effects which are in general small, not "linear" (*cf.* Ref. 16), and quite specific.

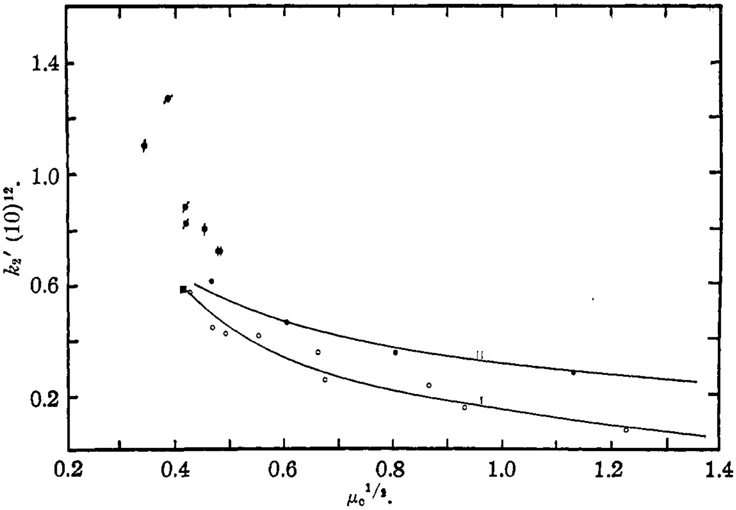

Fig. 5.—Variation of k_2' with ionic strength in the presence of Sörensen phosphate buffer. (Added salt: ○, $NaClO_4$ (Curve I); ●, Na_2SO_4 (Curve II); and ϕ, phosphate buffer only. For composition of reaction mixture designated by ■, the initial point for the curves, see Fig. 4.)

An examination of Fig. 5 will reveal that addition of sodium perchlorate (Curve I) or sodium sulfate (Curve II) decreases the value of k_2' as calculated from the values of F and k_1 for each reaction mixture. It is apparent from Equation 9, which serves to define k_2', that this constant is more complex in nature than k_1, the specific rate of the simple bimolecular Reaction 4. As in Fig. 4, the phosphate points represent the superposition of two salt effects. No matter what salt is added, the effect on k_2' is relatively much greater than the corresponding effect shown in Fig. 4 for k_1; this result might have been expected from the fact that the concentration of hypoiodite ion is governed by the equilibria, Reactions 8 and 13, and by the buffer equilibrium which regulates the activity of hydrogen ion. The salt effect on k_2' is thus the resultant of several equilibrium salt effects,[15] which may be large, and a kinetic salt effect, which is probably small.

Jones and Kaplan have observed $(\mathrm{I}^-)(\mathrm{I}_2)/(\mathrm{I}_3^-)$ to be constant for values of (I^-) below 0.3 M in solutions not saturated with iodine, and this constancy may be regarded as evidence that γ_{I^-} and $\gamma_{\mathrm{I}_3^-}$ remain proportional to each other over this concentration range. It seems probable that this proportionality will be maintained when other salts are added in moderate amount to dilute solutions of tri-iodide ion—in other words, that our use of the value $(\mathrm{I}^-)(\mathrm{I}_2)/(\mathrm{I}_3^-) = 0.00140$ at varying ionic strength is justified, and that Reaction 13 undergoes no salt effect as large as those in Fig. 5.

To determine whether these effects are due mainly to a salt effect on the equilibrium

$$\mathrm{H_2PO_4^-} \rightleftarrows \mathrm{HPO_4^{--}} + \mathrm{H^+}$$

measurements were made with a glass electrode of the hydrogen-ion activity in an equimolal Sörensen phosphate buffer solution to which other salts had been added. It was found that a_{H^+} was increased when μ_c was raised to 1 M by the addition of sodium perchlorate or sodium sulfate; the increase was greater for the perchlorate, but in both cases it was more than sufficient to explain any decrease in k_2' given by Curves I and II.

Finally, we shall consider how far our main conclusions are dependent on the empirical (and somewhat arbitrary) manner in which we have disposed of activity coefficients in the formulation of F (*cf.* Equations 9, 9a and 11). This formulation is convenient for three reasons: it employs the activity of hydrogen ion,[16] which, rather than the concentration, is given by buffer tables; it makes no assumption with regard to γ_{I^-} and γ_{IO^-}; and it is applicable to both the buffers employed. This formulation does assume, however, that substances present in the reaction system, but not properly a part of the buffer solution, do not affect the value of a_{H^+} given by the buffer tables. We have seen in the case of the phosphate

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[15] Brönsted has given the name "secondary kinetic salt effect" to the salt effect on an equilibrium (see, for example, "The Velocity of Ionic Reactions," Contemporary Developments in Chemistry, Columbia University Press, 1927). The use of the term "equilibrium salt effect" might serve to distinguish more clearly between this and a true "kinetic salt effect," such as that on k_1, which has been called a "primary kinetic salt effect" by Brönsted.

[16] By "activity of hydrogen ion" in a solution is meant the quantity (whose negative logarithm may be regarded as the P_{H} of the solution) which may be obtained from a hydrogen electrode measurement. (In this connection, *cf.* Ref. 9a.) Whether an individual ion activity has an experimental significance in moderately concentrated solutions if the kinds and concentrations of other ions are left unspecified is another question.

buffer (*cf.* Fig. 5) that this assumption is not valid. In the case of the acetate buffer, however, the added iodide is so small (*cf.* Table Ia) that the value of a_{H^+} is probably unaffected by its addition. The conclusions drawn from Table Ia are therefore uncertain only to the extent to which changing (Ac^-) from 0.1 (Nos. 112, 125) to 0.9 *M* (No. 88) affects γ_{I^-} and γ_{IO^-}.

That this effect cannot be large enough to cause a mistake in the kinetic interpretation of the data is evident from the following considerations. If, in the thermodynamically exact formulation of *F*, the buffer equilibrium

$$HAc \rightleftharpoons H^+ + Ac^-$$

is included, Equation 11 becomes

$$F_{\text{exact}} = \frac{\gamma_I - \gamma_{IO} - (\gamma_{HAc})^2}{(\gamma_{Ac^-})^2\ \gamma_{I_2}} \frac{(I^-)^2(HAc)^2}{(Ac^-)^2(I_2)} (K_{HAc})^2 \qquad (11a)$$

where K_{HAc} is the dissociation constant of acetic acid. Although the factor involving the activity coefficients is probably not equal to unity even in moderately dilute solutions, it is obvious that its value should change very little when the ionic strength is changed. This consideration leads to the very simple result that the concentration term, which we shall call F_c, in Equation 11a should be constant[17] for all experiments in Table Ia with a_{H^+} below 10^{-4} *M*. In Table II are listed values of F_c calculated for the experiments in Table Ia by use of the value $K'_{HAc} = 2.55$ (10^{-5})[18] for the buffer solution employed in Nos. 112 and 125, Table Ia.

TABLE II

RECALCULATION OF MEASUREMENTS IN TABLE Ia[a]

Expt.	112 125	124 111	123 110 97	96	95	87	91	90	89	93	92	88
$\frac{(HAc)}{(Ac^-)}$	$\frac{90}{10}$	$\frac{85}{15}$	$\frac{80}{20}$	$\frac{70}{30}$	$\frac{60}{40}$	$\frac{50}{50}$	$\frac{40}{60}$	$\frac{30}{70}$	$\frac{20}{80}$	$\frac{15}{85}$	$\frac{10}{90}$	$\frac{8.8}{91.2}$
F_c	5.0	4.2	3.6	3.4	3.6	3.8	3.5	4.0	4.0	3.5	3.1	2.7
F	4.9	4.3	3.6	3.5	3.6	3.7	3.2	3.5	3.2	2.7	2.1	1.8

[a] Average values are given for duplicate experiments.

The constancy of the F_c values is all that could be expected; at the higher acetate-ion concentrations they are more constant than the *F* values themselves. The approximate formulation of *F* in Equation 11

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[17] Abel [*Z. physik. Chem.*, **122**, 49 (1926)] has pointed out that a similar simplification is possible in a study of the oxidation of iodide by iodate ion in acetic acid–acetate ion buffer solutions.

[18] Ref. 9a, Table II. The *apparent* dissociation constant is defined by the equation $K'_{HAc} = a_{H^+}(Ac^-)/(HAc)$; this value, rather than the *absolute* value $K_{HAc} = 1.86$ (10^{-5}), must be used if agreement with *F* as calculated for Nos. 112 and 125, Table Ia, is to be obtained. The use of the absolute value would not affect the above argument; for this relates only to the trend in F_c, which is unaffected by the value of K_{HAc} chosen.

therefore suffices for purposes of establishing a mechanism. A thermodynamically exact formulation of the steady state function cannot be given, however, until more knowledge is available regarding the activity coefficients concerned.

Conclusion

A re-investigation of the catalytic decomposition of hydrogen peroxide by the iodine–iodide couple has confirmed the mechanism previously assigned to the decomposition at the steady state, and has demonstrated its validity over a much greater concentration range. Although the results obtained differ somewhat from those of Abel, these differences are not great enough to explain why his value for the specific rate of the iodine hydrolysis is smaller by several powers of ten than the lower limit deduced for this constant from related reaction systems. Preliminary experiments indicate that the solution of this difficulty may be found in the investigation of Reactions 7 and 19 at a distance from the steady state.

The author wishes to thank Mr. L. H. Donnally of this Laboratory for making the glass electrode measurements.

Summary

1. Measurements of the rate at which hydrogen peroxide is decomposed at 25° by the iodine–iodide couple yielded the value $k_1 = 0.69 \pm 3\%$ for the specific rate of the reaction

$$I^- + H_2O_2 \xrightarrow{k_1} IO^- + H_2O \qquad (4)$$

over a 10^3-fold range of iodide concentrations.

2. Subject to certain restrictions, the steady state function for this decomposition was found to be

$$F = 3.5(10^{-12}) + 1(10^{-8})a_{H^+} \text{ at } 25^\circ \qquad (15)$$

3. By combining rate, steady state, and equilibrium data, the specific rates at 25° for the reactions

$$IO^- + H_2O_2 \xrightarrow{k_2} I^- + H_2O + O_2 \qquad (7)$$

and

$$HIO + H_2O_2 \xrightarrow{\kappa_2} H^+ + I^- + H_2O + O_2 \qquad (19)$$

were computed to be, respectively, $k_2 = 4(10^{11})$ and $\kappa_2 < 2(10^4)$. The value of κ_2 is much less accurate than that of k_2.

4. The reaction system has been studied over a series of ionic strength values produced by the addition of various salts.

5. For values of a_{H^+} below 10^{-4} *M*, only Reactions 4 and 7 need be assumed to explain the decomposition of hydrogen peroxide by the iodine–iodide couple at the steady state. As a_{H^+} is increased, Reaction 19 plays an increasingly important role; at the steady state, however, the absolute rate of Reaction 4 always equals the combined absolute rates of Reactions

7 and 19. This mechanism will explain the catalysis below the value of a_{H^+} at which oxidation of iodine by hydrogen peroxide begins.

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THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA

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RECEIVED DECEMBER 9, 1931 PUBLISHED MAY 7, 1932

The mechanism of the apparently simple photochemical decomposition of ammonia by ultraviolet light is still far from being settled. The reaction has been studied by Warburg and by Kuhn in light of wave length 2025–2140 Å. The former[2] obtained a quantum yield of 0.25, whereas the latter[3] found an average of 0.45 molecule of ammonia decomposed per quantum of light energy absorbed. In the far ultraviolet, 1600–1900 Å., the quantum yield reported by Kassel and Noyes[4] is 0.69 ± 0.24. These quantum yields have been calculated on the assumption that the photochemical decomposition follows the equation

$$2NH_3 = N_2 + 3H_2 \tag{1}$$

However, Bates and Taylor[5] state that the products of decomposition contain 96% hydrogen and 4% nitrogen and express the view that hydrazine is formed, some of which may subsequently decompose. Recently, just as this work was completed, Koenig and Brings[6] reported hydrazine as a product of the photochemical decomposition of ammonia by ultraviolet light. By repeatedly flowing ammonia gas back and forth through a quartz vessel exposed to the radiation from a zinc spark for fifty hours and by continuously freezing out the hydrazine, a very minute quantity of the latter was condensed, sufficient for a qualitative test. Warburg and Kuhn determined the amount of reaction by measuring the increase in pressure, so that their low quantum yields might be accounted for by assuming that the reaction which occurs is largely

$$2NH_3 = N_2H_4 + H_2 \tag{2}$$

instead of equation (1). Kuhn found that on complete decomposition of ammonia the pressure doubled; this, however, does not prove much since hydrazine would also decompose under such treatment.

It is evident then that the composition of the gas resulting from the photolysis of ammonia should be determined under the same conditions

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[1] National Research Fellow in Chemistry.

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